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Program 7 **Hydrogen Interactions in Aluminum-Lithium Alloys**

S.W. Smith and J.R. Scully

Objective

The objective of this work is to develop a fundamental understanding of the effects of dissolved and trapped hydrogen on the mechanical properties of selected Al-Li-Cu-X alloys. We propose to: (a) distinguish hydrogen induced EAC from aqueous dissolution controlled processes, (b) correlate hydrogen induced EAC with mobile and trapped hydrogen concentrations and (c) identify significant trap sites and hydrides (if any) through the utilization of model alloys and phases.

Hydrogen Interactions in Aluminum Lithium Alloys

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This program seeks to develop a fundamental understanding of the effects of dissolved and trapped hydrogen on the mechanical properties of selected Al-Li-Cu-X alloys. We propose to (a) distinguish hydrogen induced EAC from aqueous dissolution controlled EAC, (b) correlate hydrogen induced EAC with mobile and trapped hydrogen concentrations, and (c) identify significant trap sites and hydride phases (if any) through utilization of model alloys and phases. A review of the literature indicates three experimental factors which have impeded progress in the area of hydrogen EAC for this class of alloys. These are: (i) inter-subgranular fracture in Al-Li alloys when tested in the S-T orientation in air or vacuum make it difficult to readily detect hydrogen induced fracture based on straight forward changes in fractography, (ii) the inherently low hydrogen diffusivity and solubility in Al alloys is further compounded by a native oxide which acts as a hydrogen permeation barrier; these factors complicate hydrogen detection and measurement, and (iii) hydrogen effects are masked by dissolution assisted processes when mechanical testing is performed in aqueous solutions. This program will attempt to circumvent these experimental barriers through the use of novel breaking load, hydrogen analysis, and metallurgical techniques. The intended approach and current program status is reviewed.

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Sponsored by NASA-Langley Research Center. Pending support from the Alcoa Technical Center Foundation Program

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Experimental Problems associated with Investigation of Hydrogen Effects in Al-Li-Cu-X Alloys

1. **Problem:** Low fracture toughness is observed for aged Al-Li-Cu-X alloys stressed in the S-T orientation. Intergranular and inter-subgranular fracture occurs in air or in vacuum making it difficult to detect hydrogen asssisted fracture on the basis of fractography. **Solution:**. Test specimens in L-T orientation after appropriate aging to produce shear band cracking in air or vacuum.

2. **Problem:** Low hydrogen diffusivity and solubility in aluminum alloys is compounded by an oxide permeation barrier. These factors make hydrogen analysis difficult. **Solution:** Use thermal desorption spectroscopy and Pd coated samples.

3. **Problem:** Aqueous EAC response may be dominated by dissolution assisted processes even during cathodic charging. This tends to mask hydrogen effects. Fractographic features distorted by dissolution. **Solution:**Use modification of method originally described by *Gruhl and co-workers* or use Pd coated breaking load samples.

Approach

1. Age alloys to produce shear band fracture in air.

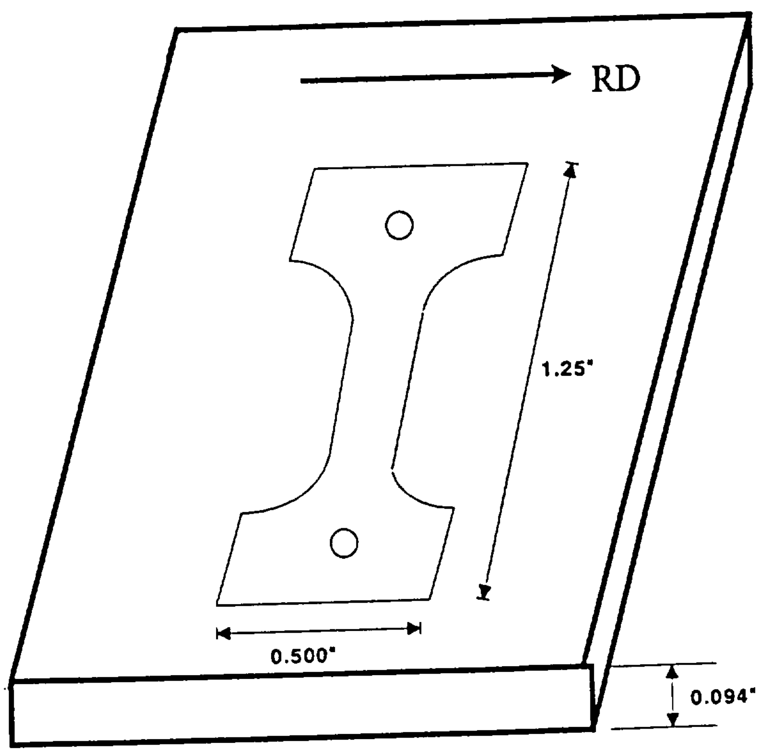
2. Perform modified breaking load and slow strain rate tests using pre-charged Al-Li-Cu-X alloys in L-T orientation. Use Pd coated samples with native oxide removed by sputter etching. Use alloy with a known hydrogen response (i.e. 7075-T6) as a control.

3. Analyzed fracture surfaces using "advanced" methods

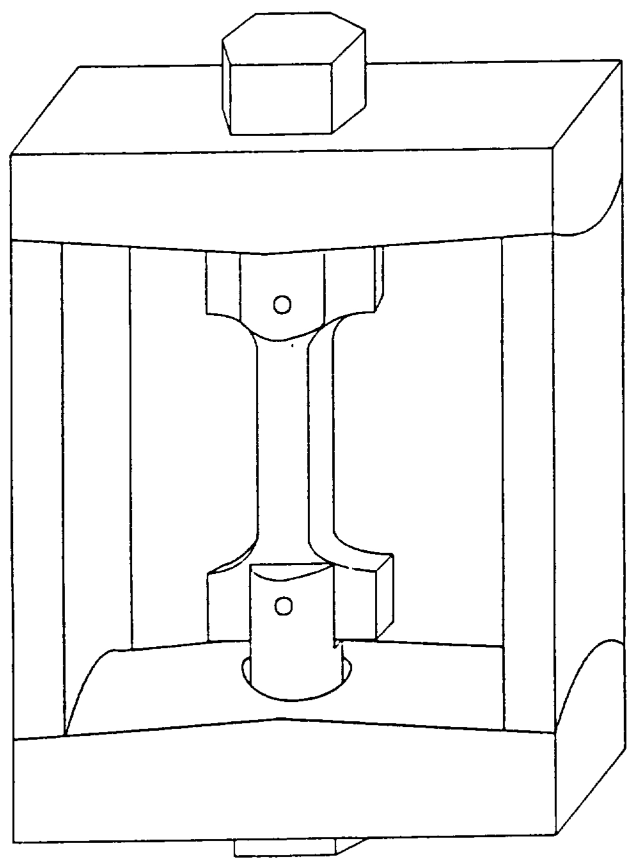
4. Conduct hydrogen analysis on hydrogenated model alloys as well as Al-Li-Cu-X alloys specimens:

   a) Modified Devanathan-Stuchurski permeation method
   b) Thermal desorption spectroscopy
   c) hydride detection methods
   d) nuclear methods

Fabrication of Flat Tensile Bar in L-T Orientation for Breaking Load Studies



Constant Deflection Apparatus for use in Breaking Load studies



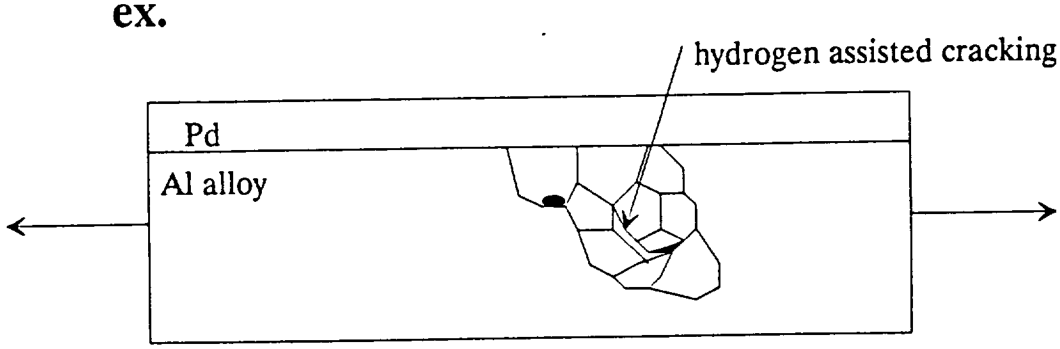
Advantages to Using Palladium Coatings

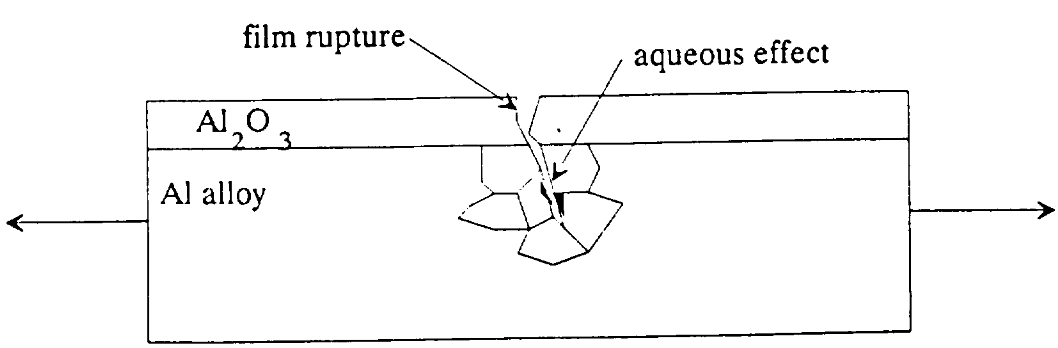
- Can remove Al_2O_3 layer, which impedes hydrogen diffusion.

- Surface of specimen will not be affected by cathodic charging.

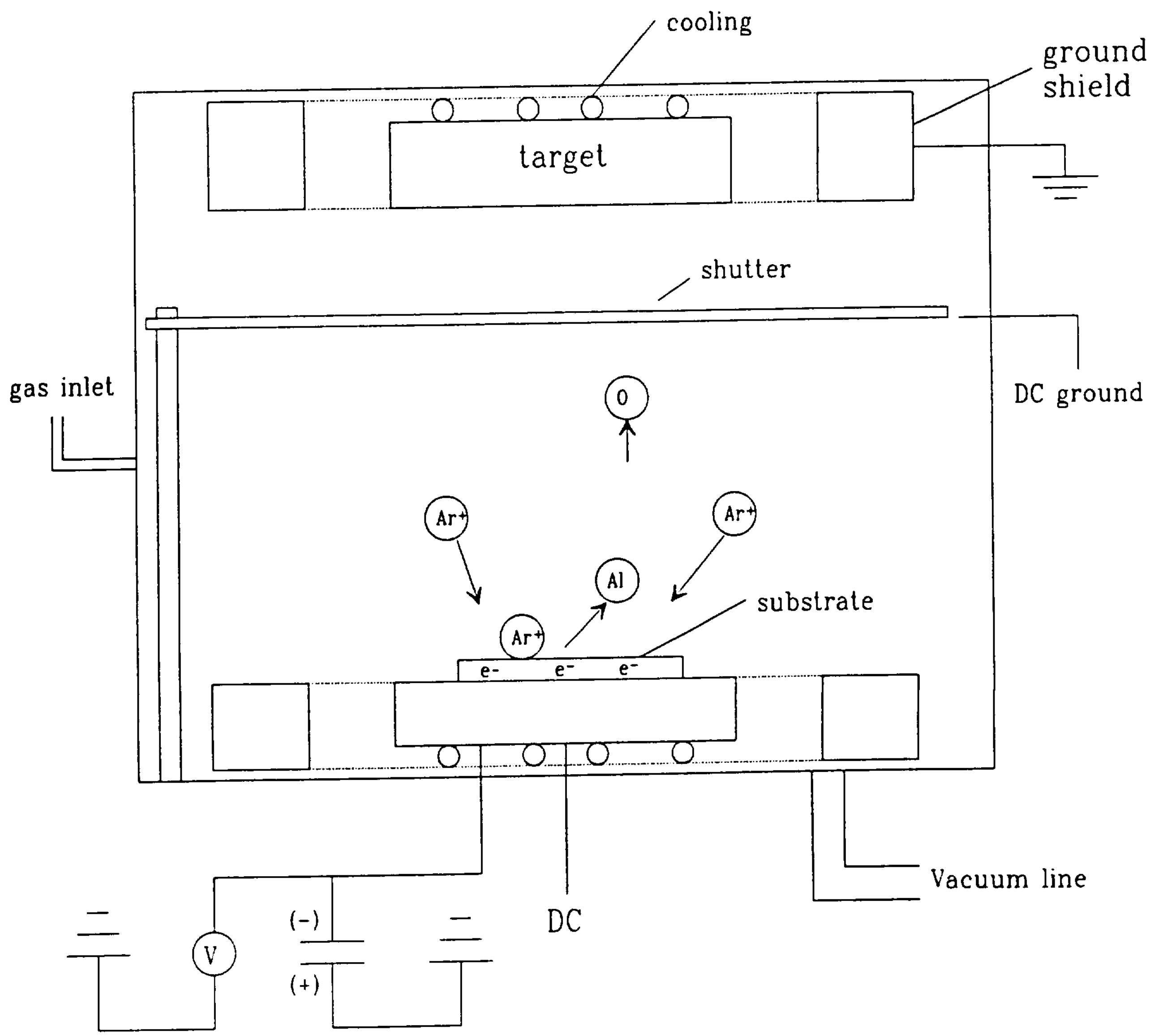
- Can distinguish between aqueous and hydrogen effects.

ex.

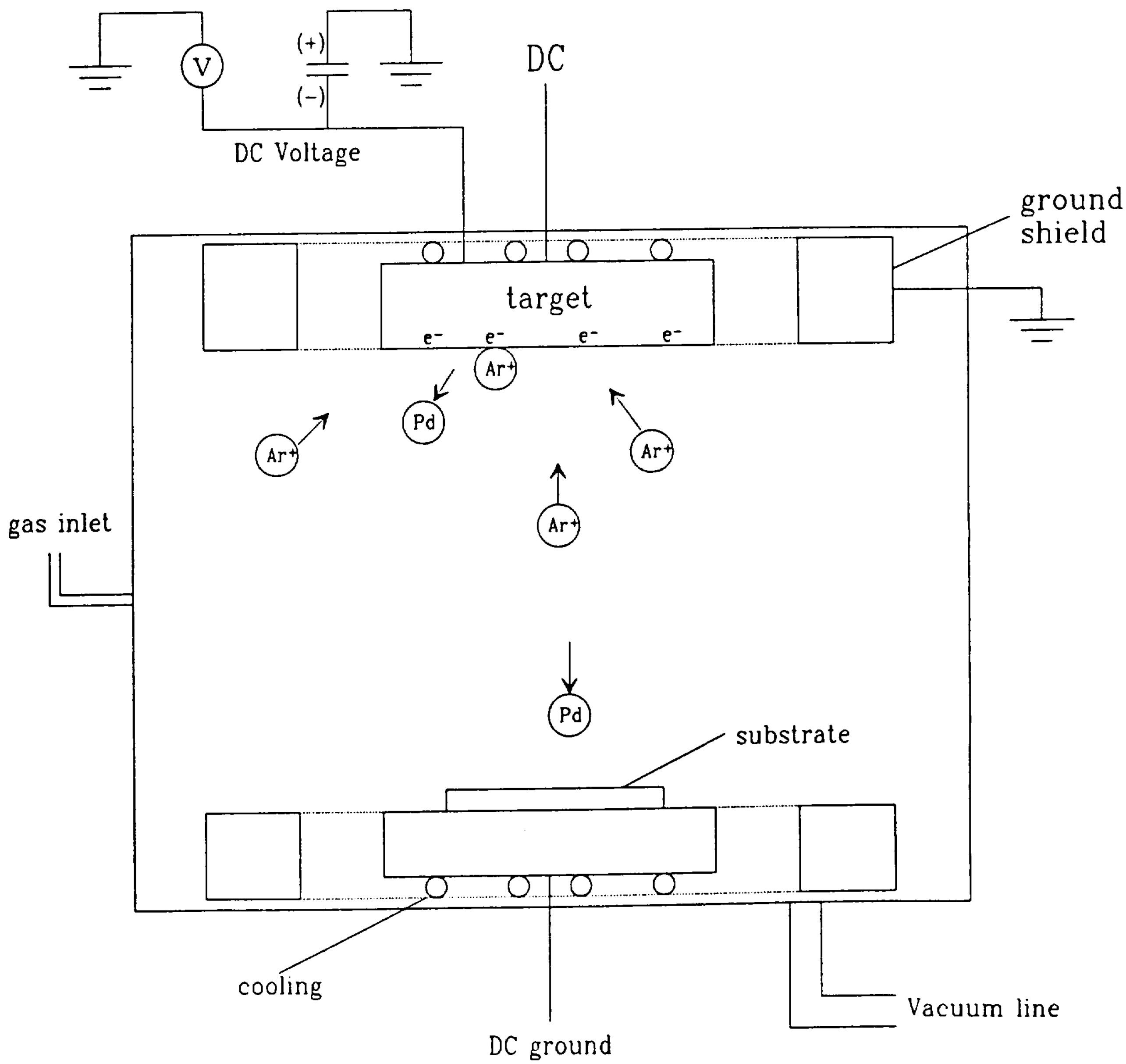




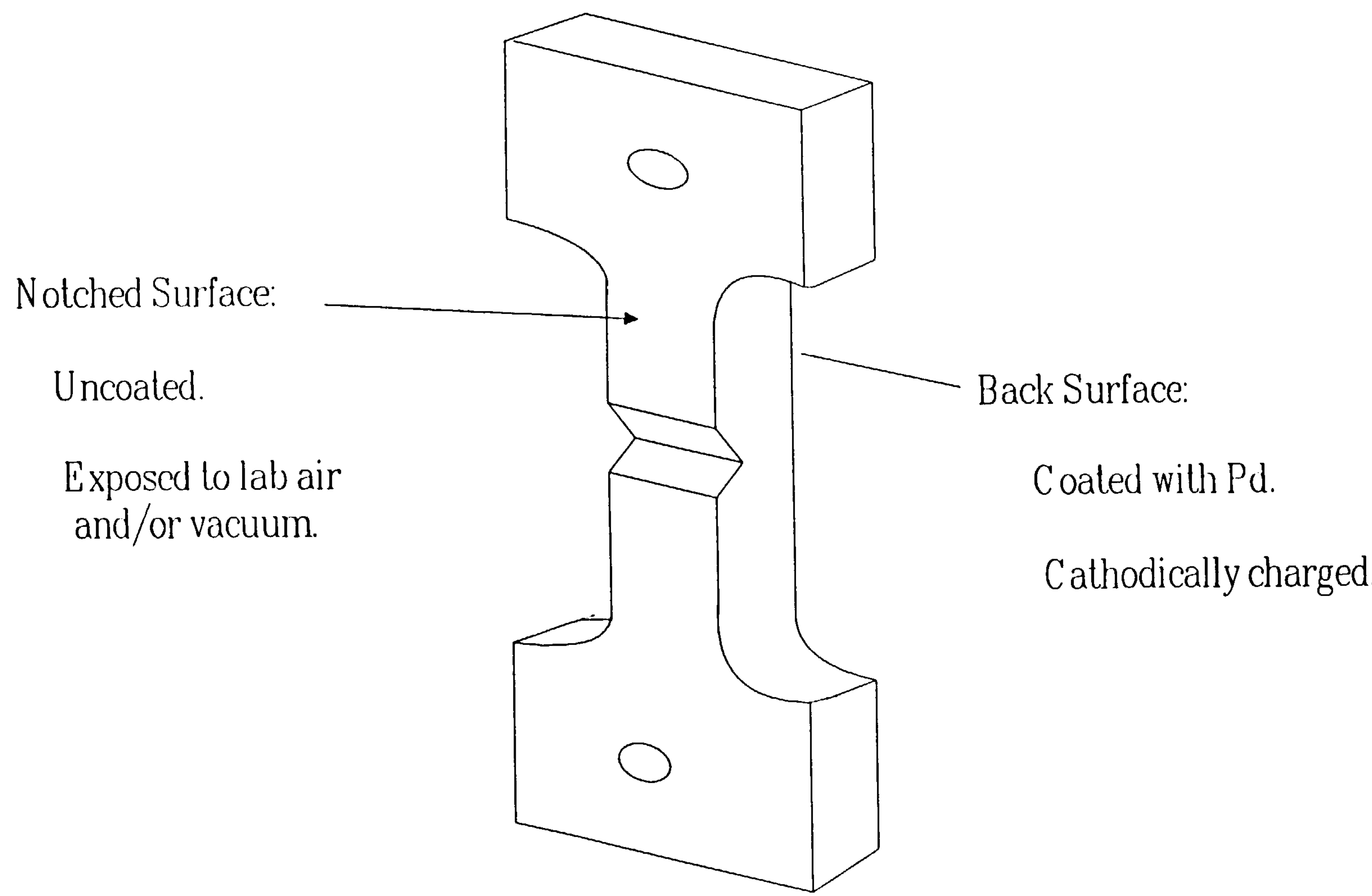
Etching of an Aluminum Alloy Substrate by dc Sputter Etching



Deposition of Palladium by dc Sputtering



Tensile Specimen for Modified Breaking Load Studies



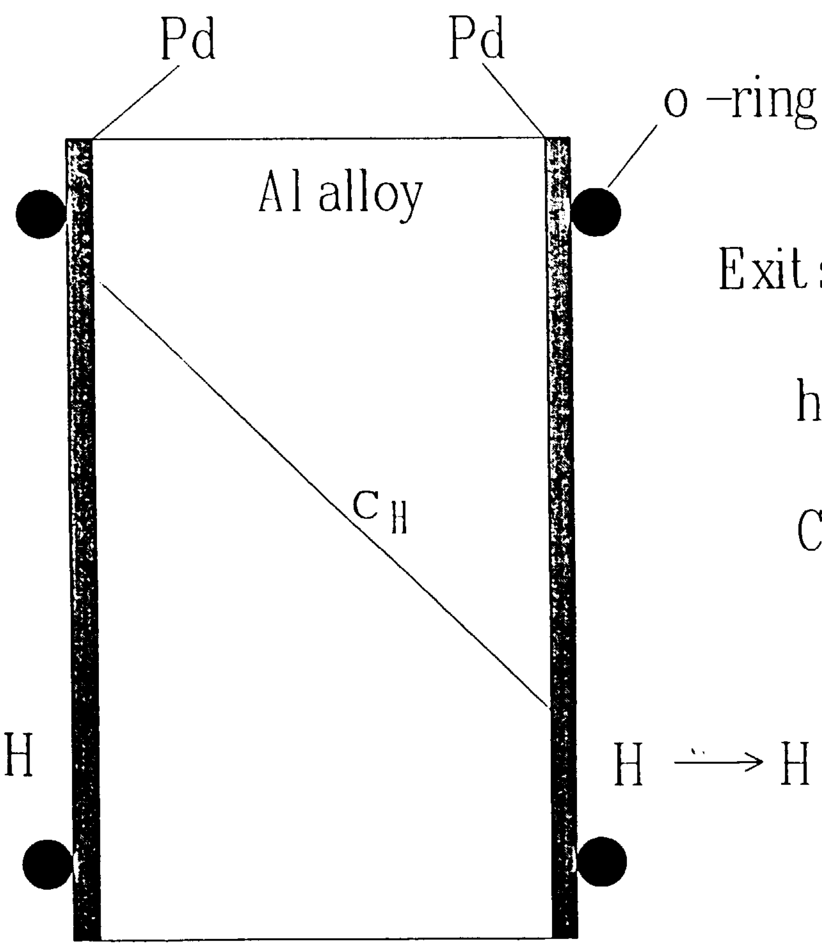
Test Matrix for Breaking Load Studies

Material	Orientation	Treatment	Fractography at Applied Load		
			50% YS	70% YS	90% YS
7075 - T6	L - T	Glove Box / Lab Air	slip band	slip band	slip band
2090 -	L - T	Glove Box / Lab Air	slip band	slip band	slip band
8090 -	L - T	Glove Box / Lab Air	slip band	slip band	slip band
7075 - T6	L - T	Cathodic Charging	to be determined		
2090 -	L - T	Cathodic Charging	to be determined		
8090 -	L - T	Cathodic Charging	to be determined		

Hydrogen Analysis Methods Pertinent to Aluminum-Lithium Alloys

Method	Advantage	Facility	Comment
Devanathan Stuchurski Permeation	Inexpensive Significant Experience	U.Va-CESE	Favors alloys with permeability and mobile H
Nuclear Reaction $^3He(d,p)^4He$	Absolute conc. depth profile used for Al	Sandia	Not readily avail. trapped+mobile D must use D_2O
Thermal Desorption Spectroscopy	relative conc. Spectroscopic assess trap strength	U.Va-CESE	proven for Al-Li must use D_2O
Neutron Act. Neutron Rad.	thick samples " "	U. Va.-Nuclear	quantitative qualitative

Hydrogen Concentration Profile During Hydrogen Permeation Studies



Charging side:

hydrogen reduction

$C_H = f(n_c)$

$H^+ + e^- \longrightarrow H$

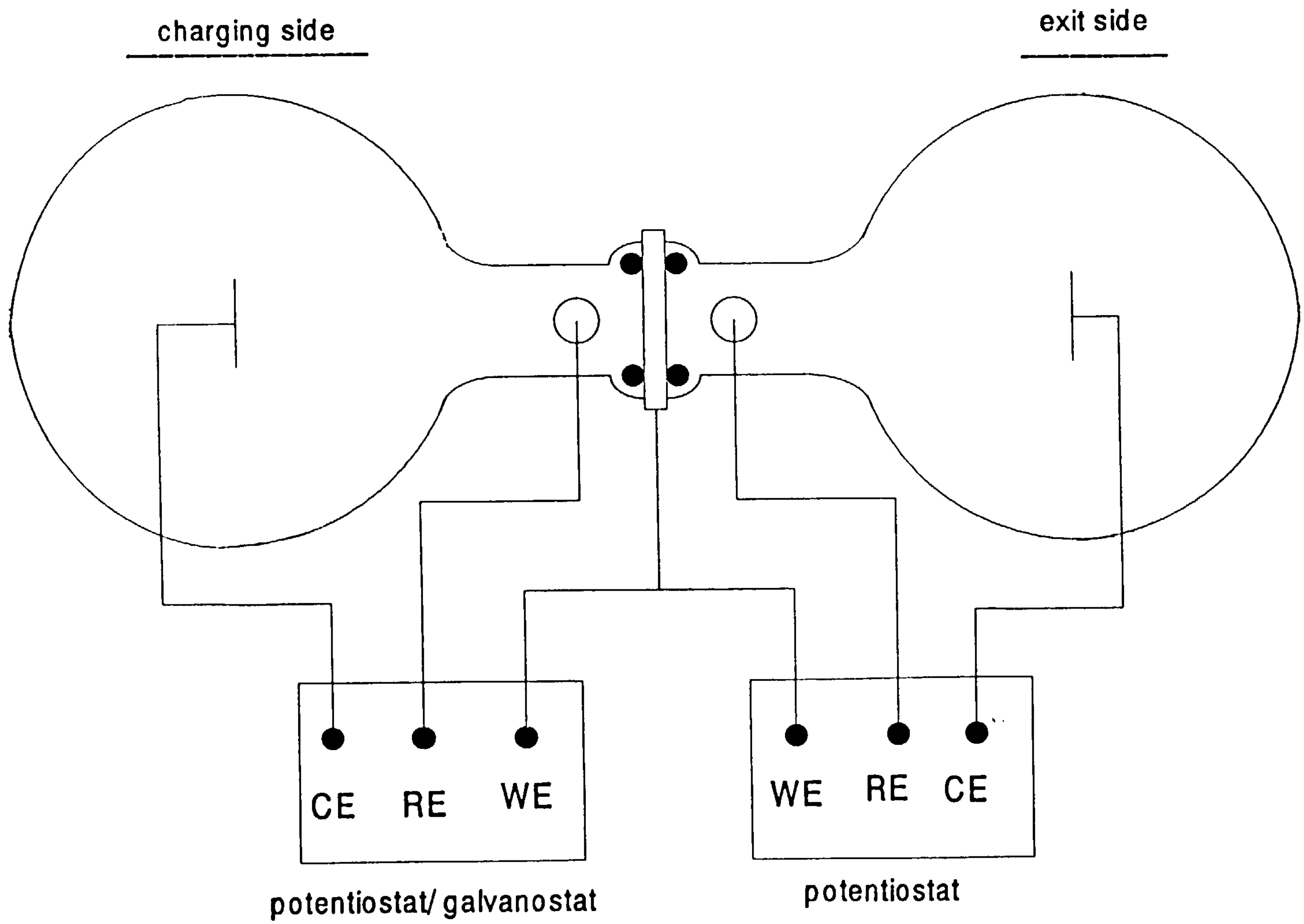
Exit side:

hydrogen oxidation

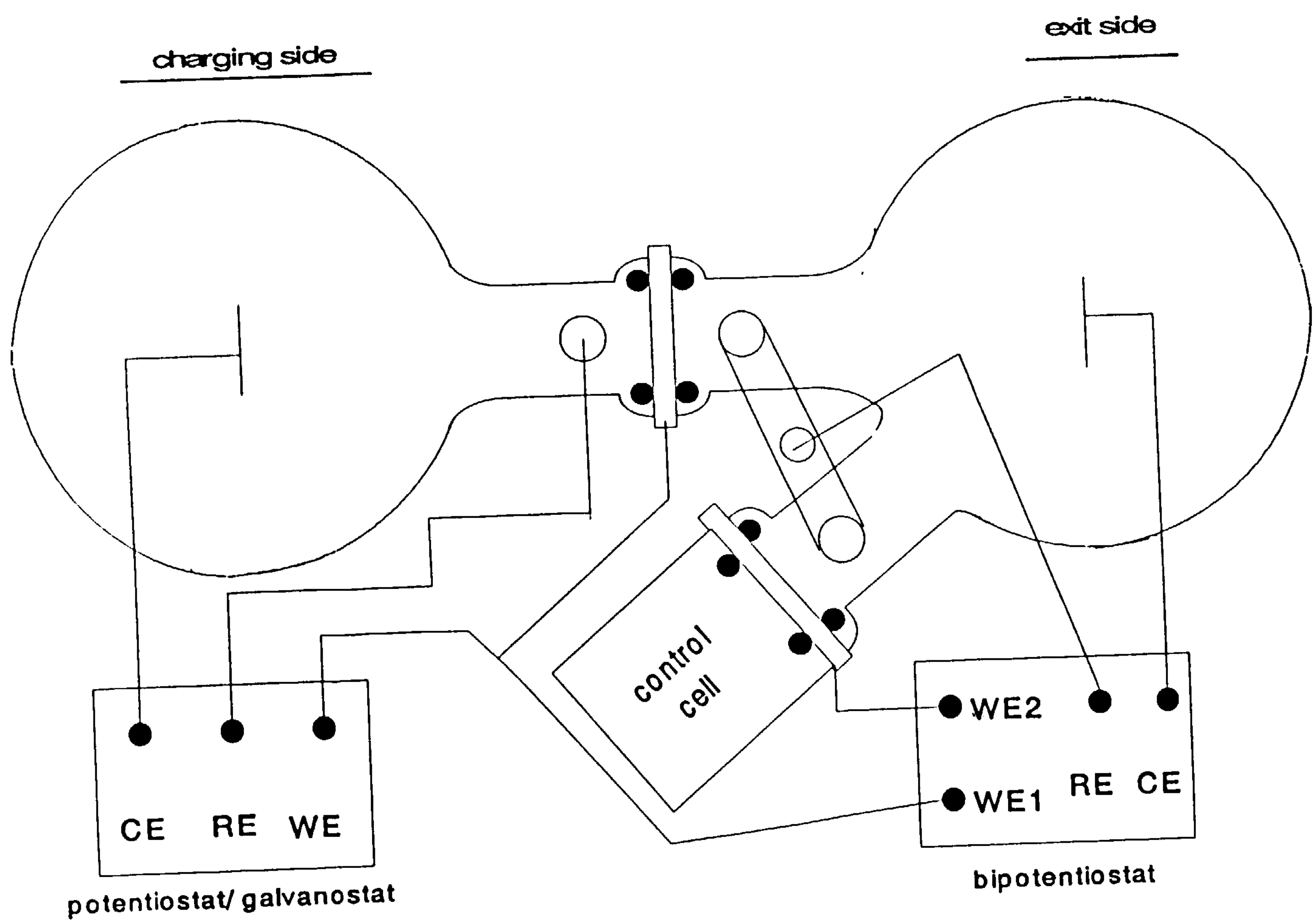
$C_H \longrightarrow 0$

$H \longrightarrow H^+ + e^-$

Schematic of Devanathan –Stachurski Permeation Cell



Schematic of Differential Permeation Cell

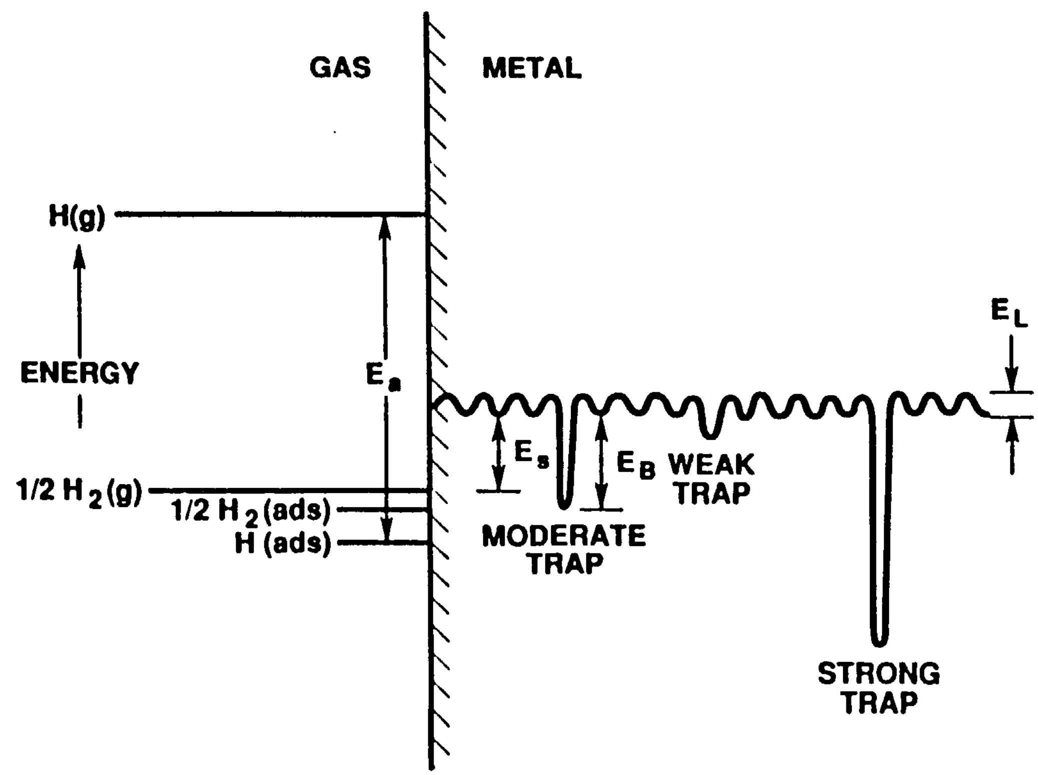


Hydrogen Transport in Endothermic Hydrogen Absorbers (Fe) is a Strong Function of The Nature and Density of Traps

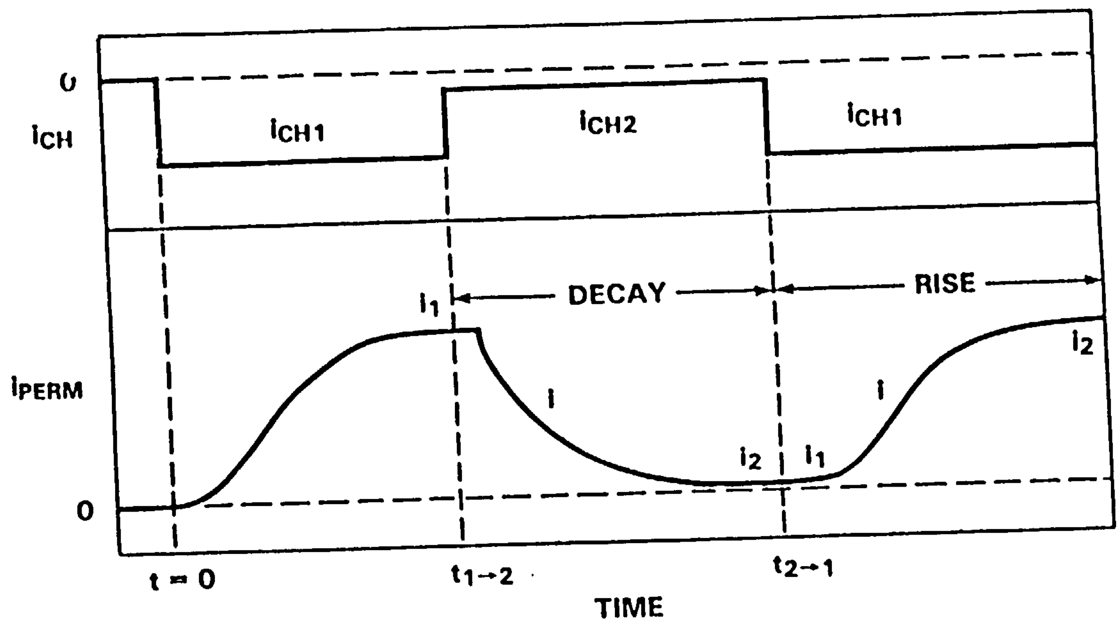
$K = N_l k_r / p_r = \exp(-E_B/RT)$, k is the trap rate, p is the release rate

N_l (lattice sites) = 2.6×10^{23} octehedral sites/cm^3 for BCC iron

$E_B > Es$ Strong Trap (~29 KJ/mole)



A Series of Permeation Rise and Decay Transients is Utilized to Separate Reversible from Irreversible Trapping



DECAY: $(i-i_2)/(i_1-i_2) = 1 - \frac{2}{\sqrt{\pi\tau}} \cdot \exp\left(\frac{-1}{4\tau}\right)$

RISE: $(i-i_1)/(i_2-i_1) = \frac{2}{\sqrt{\pi\tau}} \cdot \exp\left(\frac{-1}{4\tau}\right)$

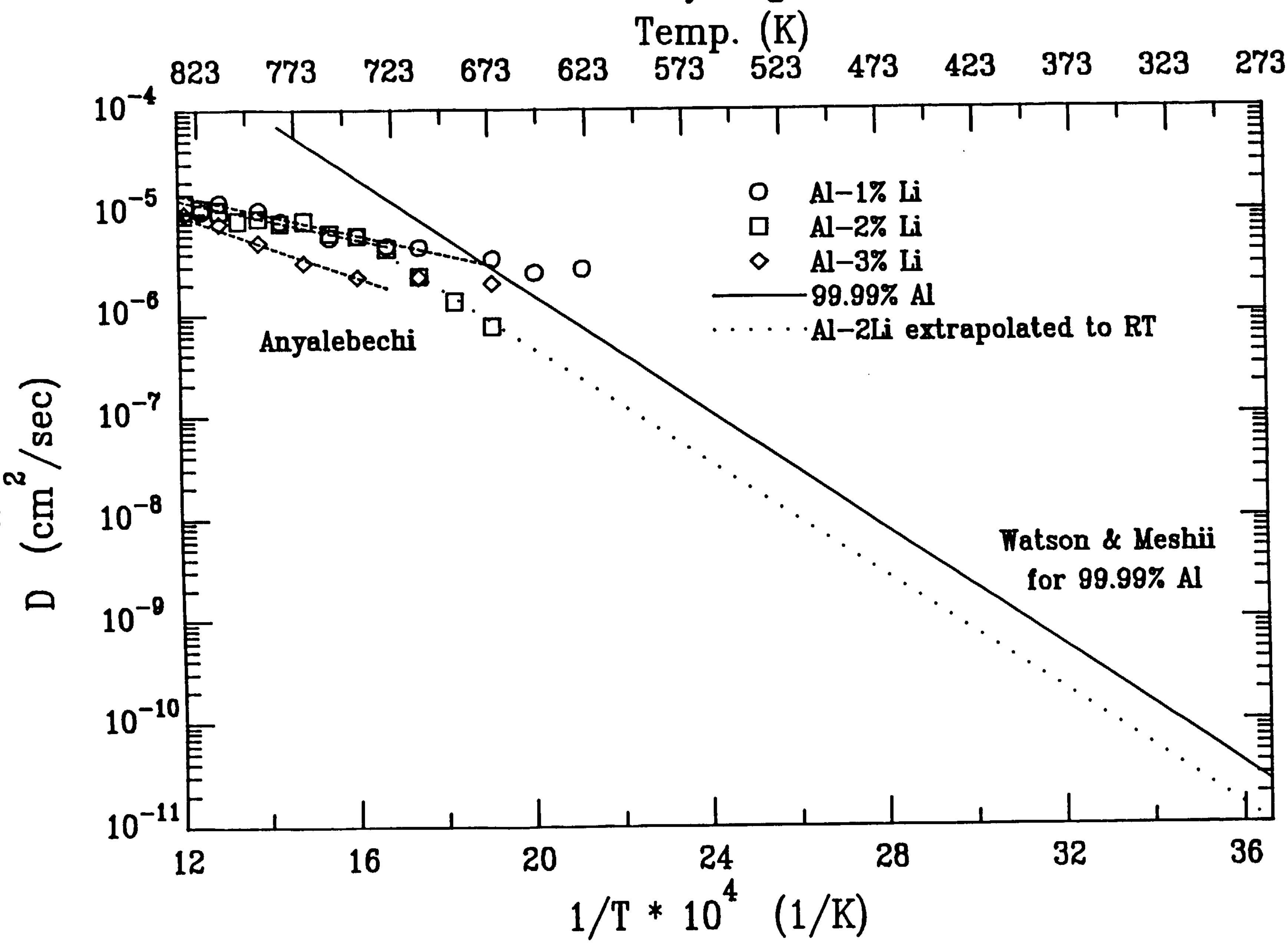
REARRANGING:

DECAY: $\log (i_1-i)\sqrt{t} = \log \frac{2F\sqrt{D}\,(C_1-C_2)}{\sqrt{\pi}} - \frac{L^2 \log e}{4D} \times \frac{1}{t}$

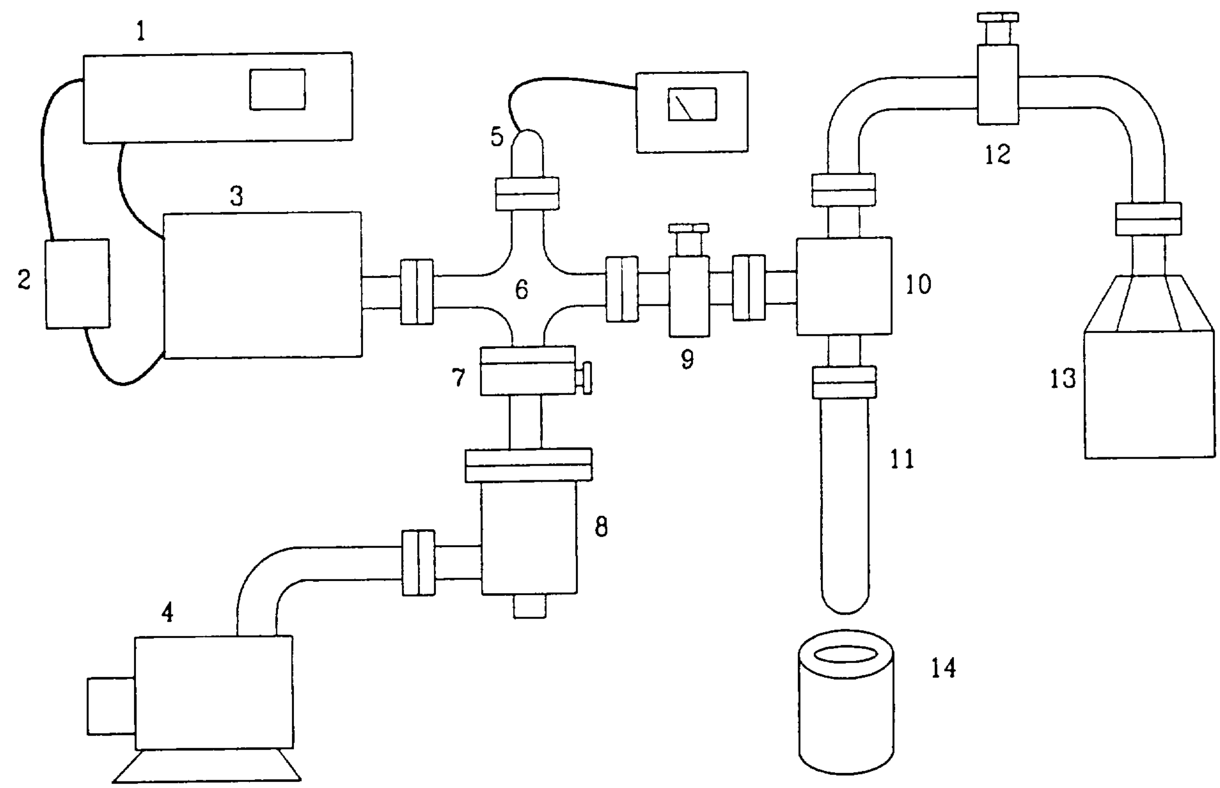
RISE: $\log (i-i_1)\sqrt{t} = \log \frac{2F\sqrt{D}\,(C_2-C_1)}{\sqrt{\pi}} - \frac{L^2 \log e}{4D} \times \frac{1}{t}$

WHERE: $\tau = Dt/L^2$

Diffusion coefficient of Hydrogen in various Al alloys

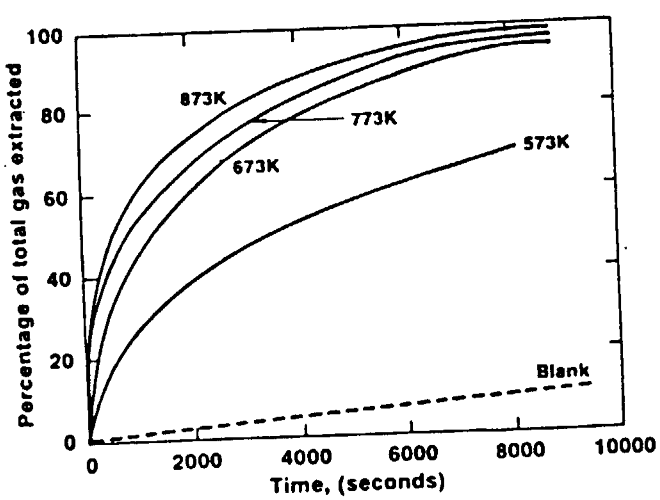


Design of Thermal Desorption Spectroscopy system

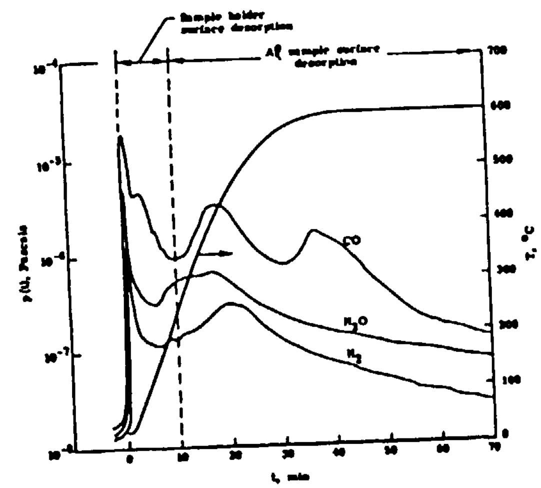


(1) Controller to quadrapole mass spectrometer. (2) RF power supply. (3) Quadrapole mass spectrometer. (4) Roughing pump. (5) Ionization gauge. (6) Analysis chamber. (7) Gate valve. (8) Turbo-molecular pump. (9) Valve. (10) Switching valve. (11) Specimen chamber. (12) Valve. (13) Sorption pump. (14) Specimen Heater.

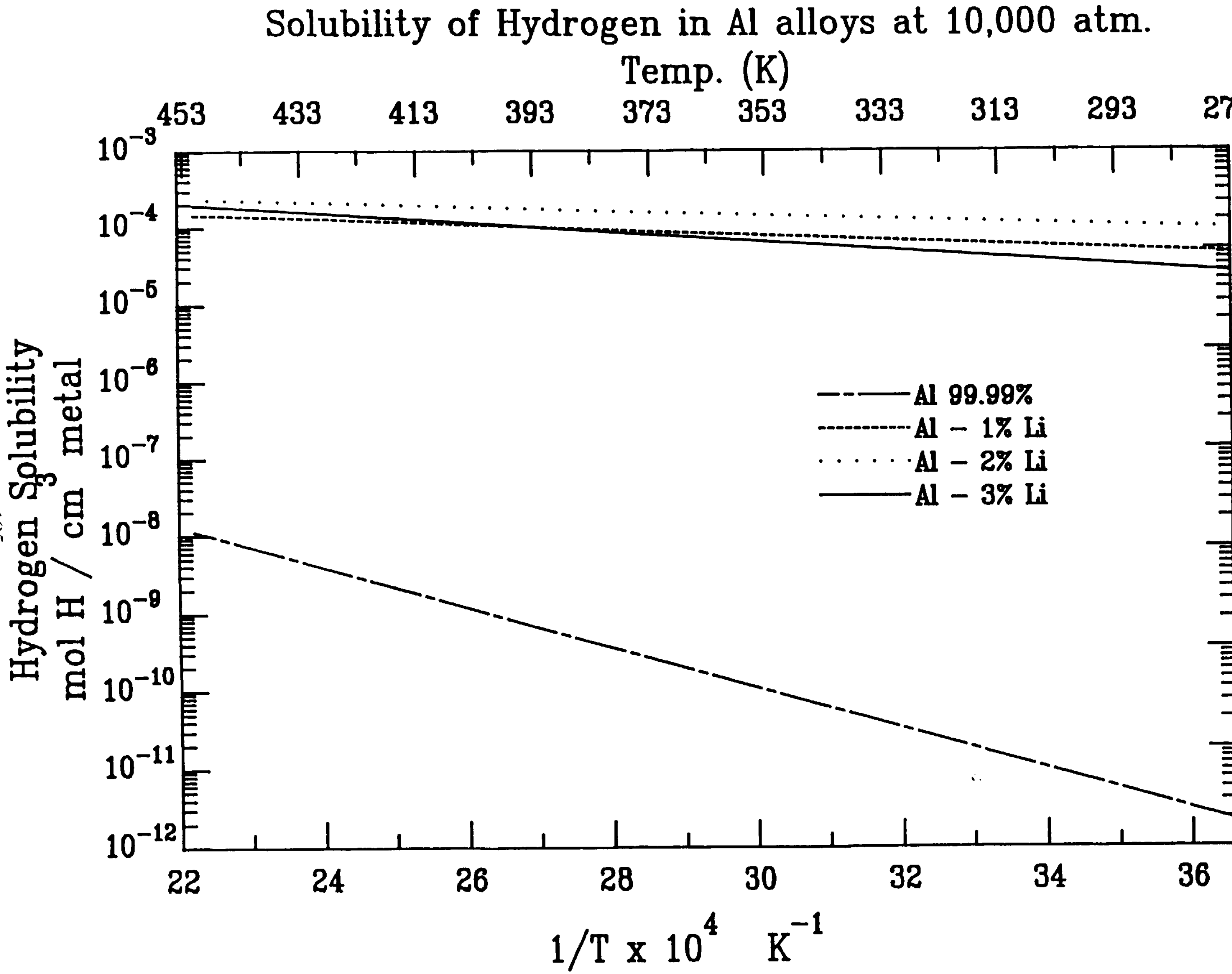
Thermal Desorption Spectroscopy Offers Several Advantages



Constant Temperature



Temperature Ramp



Solubility of Hydrogen in Al alloys at 10,000 atm.
Temp. (K)
453 433 413 393 373 353 333 313 293 273
Hydrogen Solubility
mol H / cm3 metal
10−3 10−4 10−5 10−6 10−7 10−8 10−9 10−10 10−11 10−12
Al 99.99%
Al – 1% Li
Al – 2% Li
Al – 3% Li
22 24 26 28 30 32 34 36
1/T x 10^4 K^−1

Hydrogen Trapping

Model Alloy	Exploitable Trap Site	Possible Trapping - Interaction
Al - 3Li	δ, δ', Li_{ss}	δ'-interphasal; δ,δ'-hydride; Li-solute
Al - 3Cu	θ', θ'', θ, Cu_{ss}	θ'',θ'-interphasal; θ-void
Al - Li- Cu	δ', T_1, T_2	δ',T_1,T_2-hydride; T_1-interphasal; T_2-void
T_1	T_1	T_1-hydride
Al	g.b., vacancies voids, microvoids	interfacial, point defects, voids
Al - Zr	β, β'	β-void; β'-interphasal; β,β'-hydrides
Al_3Zr (β')	β'	β'-hydride
Al - Li - Zr	δ' coats β'	interphasal; δ',β'-hydride

Program Status - June 1991

1. Hydrogen permeation cells assembled. Thin foils must be prepared.

2. Breaking load configuration built and tested. Specimen exposures to begin this summer.

3. Thermal desorption system in design stages. Equipment purchases to follow.

4. Hydrogen evolution reaction kinetics studies to be undertaken in July to ascertain hydrogen production capability of model alloys and phases.